

ROME LABORATORY/ ERXE
Final Technical Report
12/17/96

Quantum Dots: The Next Generation
of Electronic Phosphors

Timothy J. Driscoll, Ph.D.

Spectra Science Corporation
155 S. Main Street
Providence, RI 02903

Distribution notice to be selected by Contract Monitor

ROME LABORATORY
HANSCOM AIR FORCE BASE, MA 01731-3010

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

19961220 079

DXC QUALITY INSPECTED 1

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 12/19/96	3. REPORT TYPE AND DATES COVERED SBIR Phase I Final Report 6/19 - 12/19/96	
4. TITLE AND SUBTITLE SBIR Phase I Final Report Quantum Dot Phosphors: The Next Generation of Electron Phosphors		5. FUNDING NUMBERS C F19628 - 96 - C - 0094	
6. AUTHOR(S) Timothy J. Driscoll, Ph. D. Nabil M. Lawandy, Ph. D.		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Spectra Science Corp. 155 S. Main Street Providence, RI 02903			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) RL/ERXE (Rome Labs) 80 Scott Road Hanscom AFB, MA 01731-2909		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <u>"Report developed under SBIR contract"</u> SBIR phase I results include the development of a novel, aqueous based synthesis of metal chalcogenide quantum dot phosphor materials and the development of a video rate electrically addressed lasing pixel . The development of new phosphor systems will result in improved conversion efficiencies, an increased color palette, and enhanced spatial resolution of direct view and large screen displays. Our efforts have led to the development of ZnSe quantum dots through a novel aqueous based sysnthesis. In addition to the development of the nanocrystalline materials, the phase I SBIR included the development of lasing pixel displays incorporating optical gain and scatterers. In this second,area, we have demonstrated an electrically addressed lasing pixel for large screen display applications, which uses liquid crystal technology in a flat micro-cavity laser configuration.			
14. SUBJECT TERMS LaserPaint , SSBIR Report Lasing pixels , phosphors , display , quantum dots,		15. NUMBER OF PAGES 20	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

SBIR Phase I Final Report

Quantum Dot Phosphors: The next generation of electron phosphors

Timothy J. Driscoll

Spectra Science Corp.
155 S. Main St.
Providence, RI 02903

Contents

<u>Section</u>	<u>Contents</u>	<u>Page</u>
I. Phase I Technical Objectives		2
II. Phase I Results		3
a. Development of a blue Quantum Dot Phosphor		4
b. Development of a video rate electrically addressed lasing pixel		9
III. Technical Feasibility		16

I. Phase I Technical Objective

The work in the Phase I SBIR was focused on the development of novel material solutions to the major obstacles limiting the size and picture quality of projection television systems. These basic limitations arise from the needs for brighter pixelated sources, improved color saturation, and an expanded palette which is currently restricted by broadband light sources such as lamps and phosphors. The phase I effort had a two track approach; one based on the development of novel nano-scale materials known as Quantum Dot Phosphors (QDP), and the other on the use of a scattering/gain system to create a video rate electrically addressed lasing pixel. The solution to these problems will catalyze the already rapidly growing projection display sector of the display market which represents over six billion dollars of annual sales.

II. Phase I Results

SBIR phase I results include the development of a novel, aqueous based synthesis of **metal chalcogenide quantum dot phosphor materials** and the development of a **video rate electrically addressed lasing pixel**. The development of new phosphor systems will result in improved conversion efficiencies, an increased color palette, and enhanced spatial resolution of direct view and large screen displays. Our efforts have lead to the development of ZnSe quantum dots through a novel aqueous based synthesis. In addition to the development of the nanocrystalline materials, the phase I SBIR included the development of lasing pixel displays incorporating optical gain and scatterers. In this second area, we have demonstrated an electrically addressed lasing pixel for large screen display applications, which uses liquid crystal technology in a flat micro-cavity laser configuration.

IIa. Development of a Blue Quantum Dot Phosphor

Surface passivated quantum dot phosphors provide several advantages over conventional micron sized phosphor grains. The passivation of II-VI semiconductor nanocrystals (diam. less than 5 nm) removes the high density of nonradiative surface trap sites and results in a highly correlated electron-hole pair with a greater probability of radiative recombination. The problem of surface traps in conventional phosphor grains is dealt with by creating grain sizes of 3-12 microns and using kilovolt accelerating voltages to advance the incident electrons past the surface dead layer to create electron-hole pairs. Passivated nanocrystal phosphor grains operated at lower excitation energies are expected to minimize the amount of electrical energy needed to power devices.

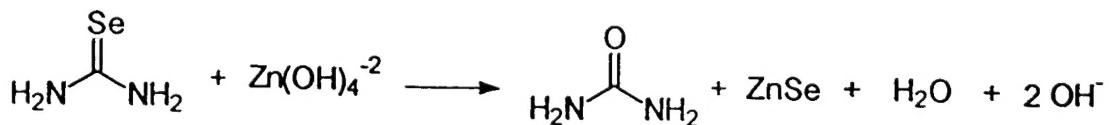
Another drawback of conventional phosphors is the lower conversion efficiencies for large screen displays where the excitation current density may be one to two orders of magnitude greater than in direct view CRTs. These efficiencies are limited by the high excitation behavior of the current blue phosphor, Ag:ZnS, whose conversion efficiency decreases as the phosphor temperature increases. Surface passivated quantum dot phosphors will allow for lower accelerating voltages and thinner screen coatings. The thinner quantum dot phosphor layer will be easier to cool reducing the effects of thermal quenching. In addition, the small size of the nanocrystal phosphor grains will improve the spatial resolution of specialty displays which are limited by the current micron sized particles.

The company's first commercial target for Quantum Dot materials is the development of a blue phosphor to replace the currently used Ag:ZnS. The formation of ZnSe quantum dots with a narrow size distribution has resulted in a blue phosphor with a significantly smaller bandwidth than the current Ag:ZnS. This becomes important when a color palette is created by the mixing of red, blue, and green emitting phosphors. Narrower spectral emissions (i.e. closer to monochromaticity) increase the size of the accessible palette and remove chromatic aberration produced in the combining RGB optics.

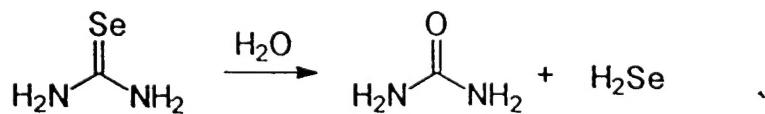
Existing methods for the synthesis of blue emitting, direct band gap, metal chalcogenide quantum dots are cumbersome and not amenable to scale up. For example, in the papers by

Murray et. al. a method is disclosed for the synthesis of cadmium selenide quantum dots.^[1] This method makes use of tri-n-octylphosphine as a coordinating solvent, with either elemental selenium or bis(trimethylsilyl)selenium as the chalcogenide donor and dimethylcadmium as the metal donor. The disadvantages of this method include the nature of the reactants, most of which need to be synthesized, the use of an expensive, air sensitive solvent, the need for high temperatures, and toxicity issues associated with the use of cadmium. Based on these issues we felt that this method would be unsatisfactory for the production of zinc selenide.

Using Phase I funds, we investigated the use of aqueous systems for the production of zinc selenide since such a method would be more readily scaled up. In order to obtain a source of selenium in the correct oxidation state we produced the required selenide by aqueous hydrolysis of seleno carbonyl compounds. We chose to take this route since compounds such as hydrogen selenide or sodium selenide are not commercially available due to their inherent instability in air. Selenourea was chosen as the starting point due to its availability and easy hydrolysis under aqueous conditions as shown below:



The hydrolysis reaction is catalyzed by both acid and base. We selected the basic route since zinc selenide is soluble in acid. Although zinc hydroxide is quite insoluble in water it can be solubilized in excess hydroxide as the zincate ion ($\text{Zn}[\text{OH}]_4^{2-}$) and therefore is suitable for a basic aqueous method. The balanced equation for the formation of zinc selenide from selenourea and zincate is shown below:



^[1] Murray C. B., Norris B. J., and Bawendi M. G., *J. Am. Chem. Soc.*, (115) 7806-7815 (1993).

Zinc selenide, due to its insolubility in aqueous media, precipitates over time in the form of quantum dots. This same method, with modification, could be useful for the formation of other metal chalcogenides as well.

Photoluminescence of the aqueous ZnSe quantum dots revealed a narrow (22 nm), blue shifted luminescence centered at 435 nm. The emission shift can be attributed to the quantum size confinement of the nanocrystals which were measured by X-ray diffraction to be 5 nm in diameter. The nanocrystals were dried and the photoluminescence measurements repeated in order to confirm that the quantum dots did not agglomerate upon drying or degrade upon contact to ambient conditions. Figure 1 displays the narrow photoluminescence of the dried ZnSe Quantum Dot phosphors compared to the much broader emission of the conventional blue phosphor ZnS:Ag. The ability to transfer the colloidal ZnSe nanocrystals into a dried powder while preserving their luminescent properties indicates that the quantum dots are passivated. Since the current synthesis does not include an explicit passivation step, it is believed that the nanocrystals are self-passivating through the formation of a surface oxide layer while still in solution.

In addition to synthesizing passivated ZnSe quantum dots, we have recently observed an increase of nearly one order of magnitude in the luminescence of the quantum dots upon exposure to UV radiation from a Xenon lamp. Figure 2 displays the growth in luminescence versus exposure time. The UV exposure is believed to increase further the degree of passivation of the nanocrystal surface.

Our work towards the development of a blue Quantum Dot phosphor has attracted a great deal of attention from Sony Corporation where a new Nanocrystal Phosphor Research team and laboratory have been assembled. In addition, the SBIR Phase I effort specifically on ZnSe has resulted in the filing of a patent relating to the general synthesis route described. The development of these synthesis routes has prompted Sony Corporation to send a full time researcher to work with the company for a six month period.

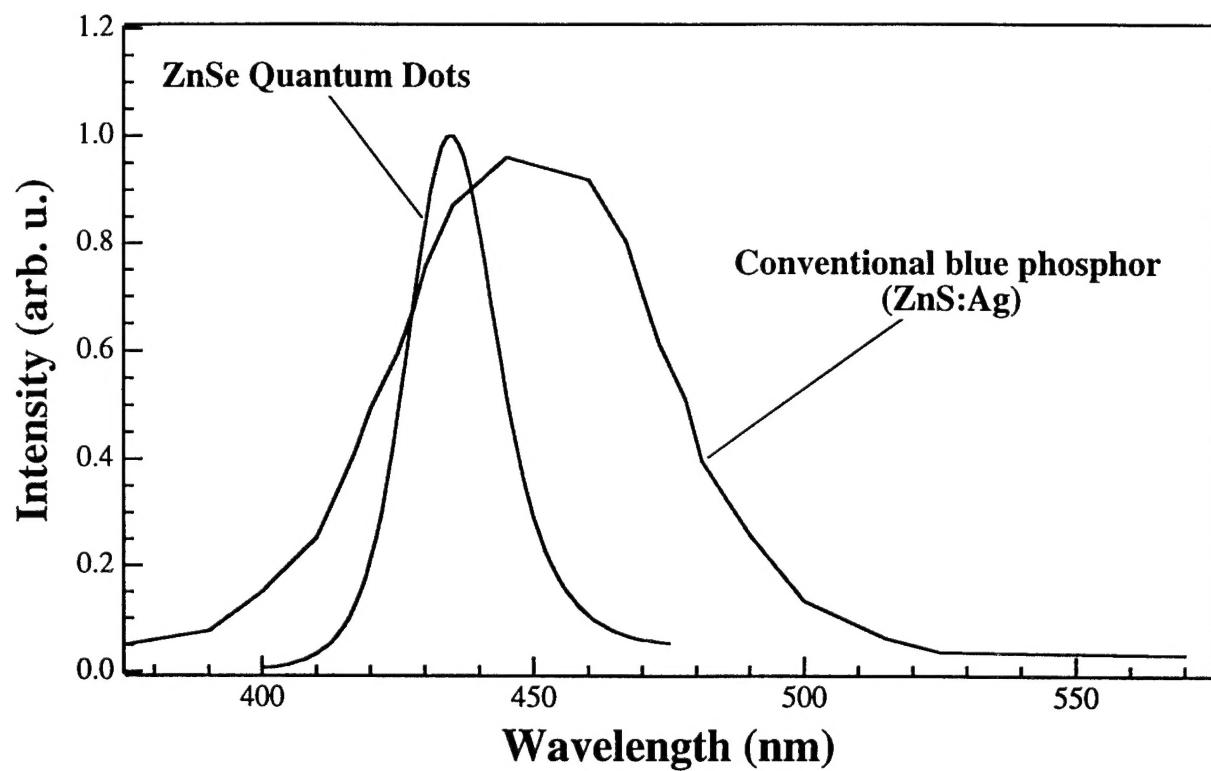


Figure 1.

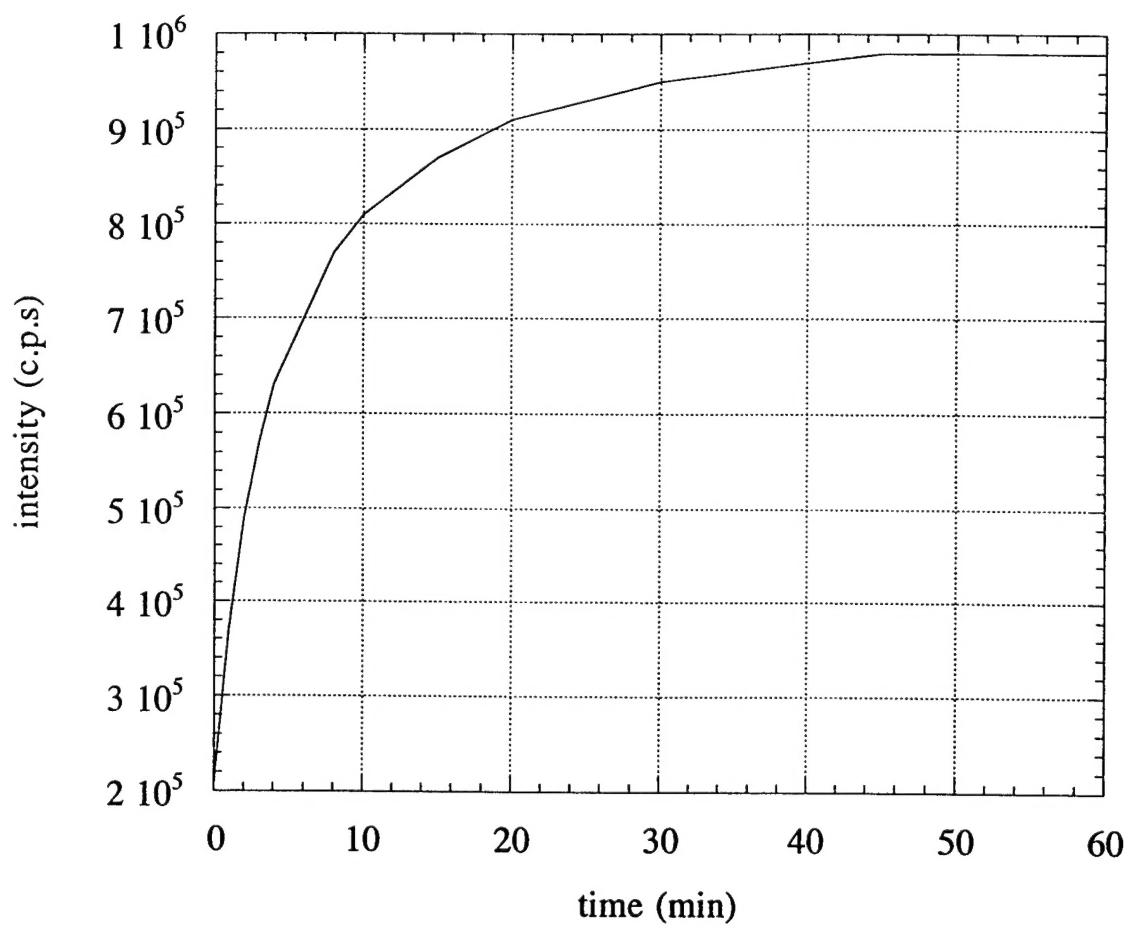


Figure 2.

IIb. Development of a video rate electrically addressed lasing pixel

Since the early 1970s several major companies (Phillips, Xerox, Daimler Benz) have spent R&D dollars aimed at the development of large screen displays created by faster scanning of high power lasers. Presently, a consortium of German companies has spent over \$100M on the development of a similar system which takes advantage of two decades of laser developments. The major motivations for this effort are the unparalleled color palette, decreased chromatic aberration, and increased brightness which result from the use of laser light for displays. This now nearly thirty year old approach, however, suffers from highly sophisticated optical scanning requirements, the free space propagation of laser beams, and the need for three independent laser sources. These complications lead to high costs, low reliability, large volume requirements, and high electrical power requirements.

Using Phase I SBIR funds targeted for the use of scattering materials in display applications, Spectra Science Corporation has developed and demonstrated a new Lasing Pixel Display Device. The concept is built upon the LaserPaint™ pixel idea that what is needed is an addressable lasing pixel rather than the scanning of large lasers. The challenge of developing a low voltage addressable lasing pixel was solved by a synergistic combination of flat screen Liquid Crystal Technology and thirty year old laser concepts.

At the heart of the Spectra Science lasing pixel is the use of a $5 \mu\text{m}$ thick Polymer Dispersed Liquid Crystal (PDLC) sandwiched inside an optical micro-cavity laser as shown in figure 3. The PDLC in the zero voltage state is highly scattering and presents a large loss for the micro-cavity laser. The application of 15 Volts allows the PDLC transmission, shown in figure 4, to increase dramatically via an index matching process. The increased transmission in turn allows the micro-cavity to reach threshold and emit laser light whose wavelength is determined by the gain medium ($< 500 \mu\text{m}$) inside. Figure 5 shows the output of the pixel vs. applied voltage, while figure 6 shows the corresponding spectrum of the light from the pixel below and above threshold. The data show that the application of a low voltage swings the output of the pixel by four orders of magnitude and its spectral output becomes a series of sharp lines confined to less than a 5 nm bandwidth!

Liquid Crystal Lasing Pixel (LCLP)

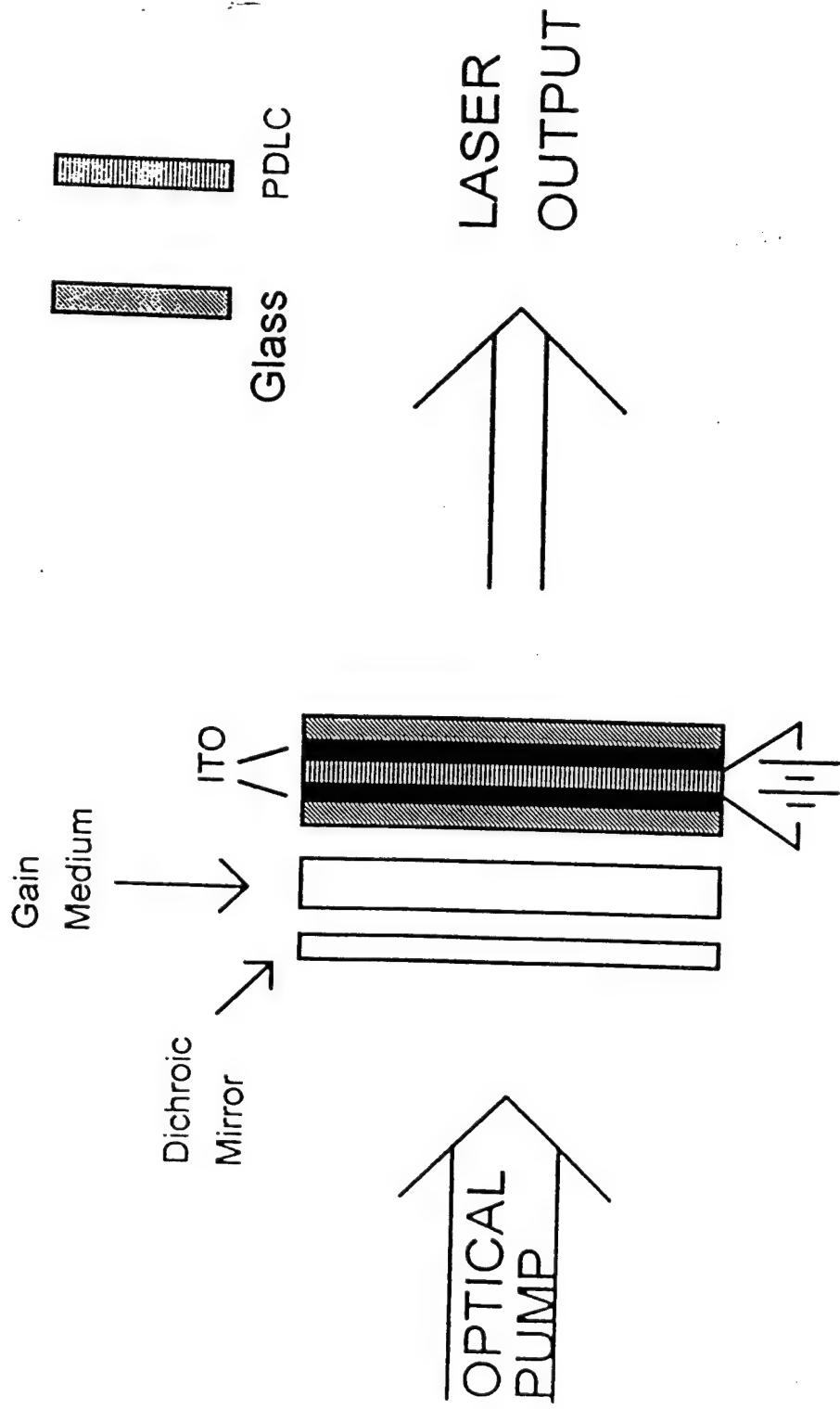


Figure 3.

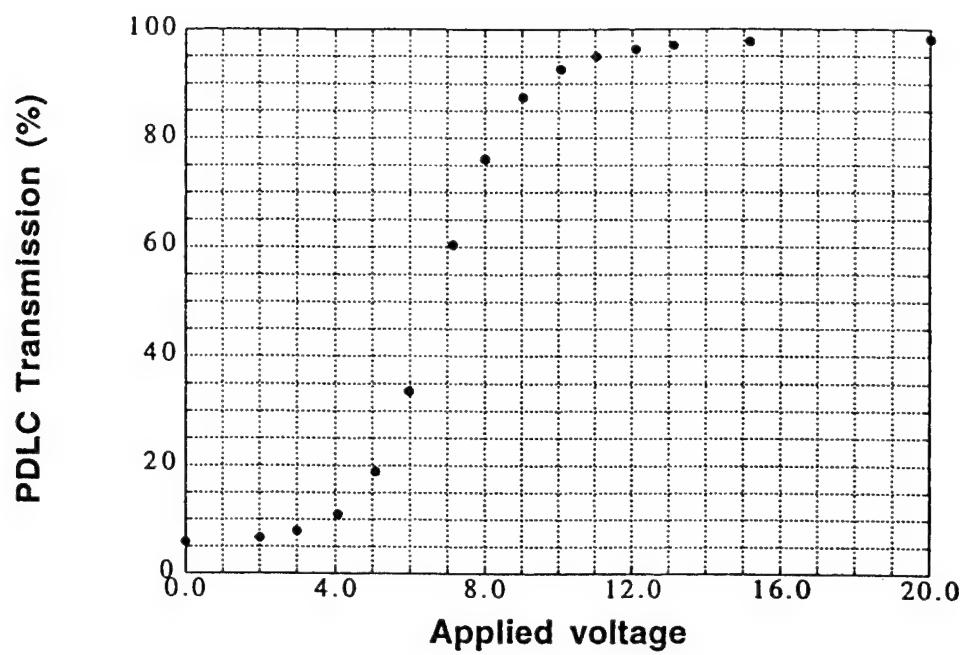


Figure 4.

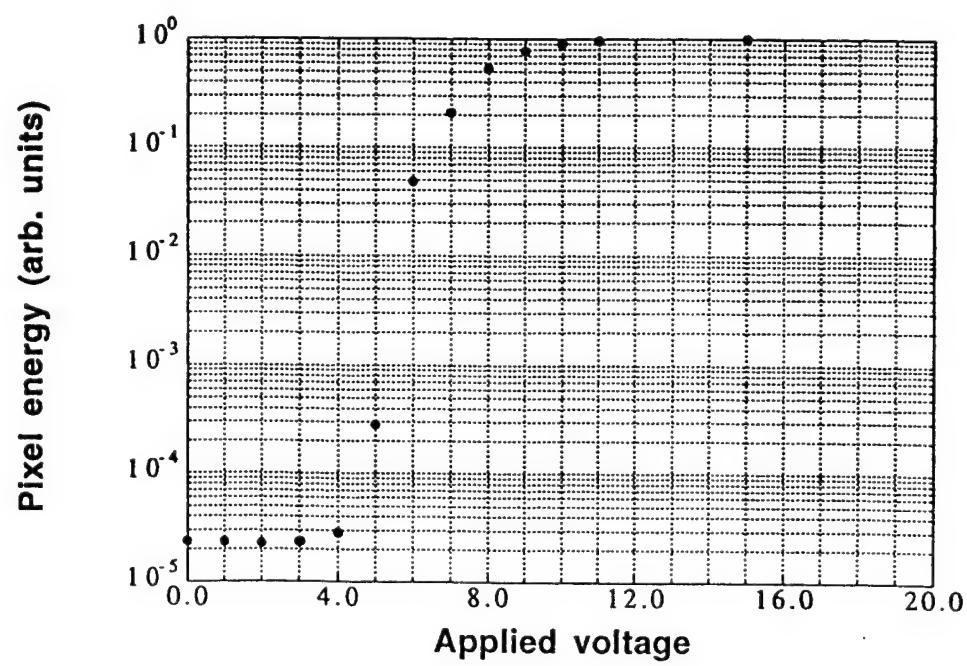


Figure 5.

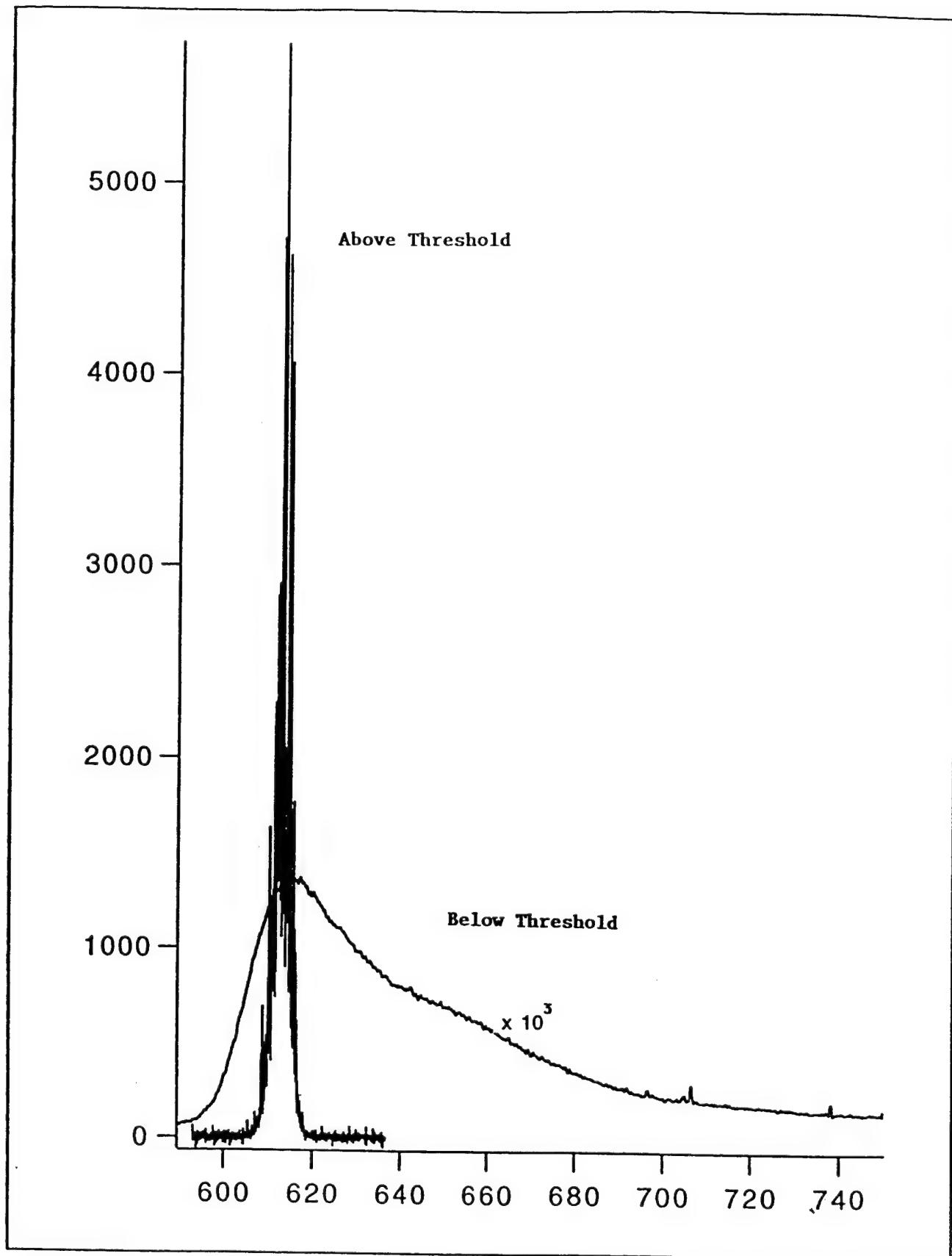


Figure 6.

The total conversion efficiency of this pixel using laser dyes as a gain media is as high as 40%. This means that 9 Watts of 355 nm light from a Q-switched frequency tripled Nd:YAG laser can result in monochrome lasing screens each capable of putting out 0.8 Watts at red, green, and blue (RGB) wavelengths. This is to be compared with current high efficiency projection CRT systems which emit of the order of 150 mW at R, G, and B with a much larger (30x) spectral emission bandwidth typical of broad band phosphors. Figure 7 shows how a single laser source can be used to drive a scan-less video rate projection display using the Spectra Science lasing pixel technology.

Spectra Science has demonstrated the lasing pixel behavior in a pixel array device. Using conventional photolithographic techniques, a 64-pixel square array PDLC device was developed and is currently being evaluated. The initial experimental results are an extremely promising demonstration that lasing pixels could be activated using direct-drive techniques. PDLC material formulations that are commercially available from EM Industries were implemented with switching voltages <10 volts and video compatible switching times. Studies are continuing on such systems to further investigate cross-coupling between pixels due to amplified spontaneous emission effects. Figure 8 shows the ITO mask used to create the 64 pixel array currently being tested.

Since the submission of the Interim Report for the SBIR Fast Track application we have made two important advances towards the final video rate lasing display. A newly designed pixel array has created addressable lines possessing an aspect ratio of 10:1. The eight separate lines which may be addressed in any combination lines are formed by addressing the complete pixel row. The other advance includes the acquisition of small scale video rate pixelated driver which will allow for the initial tests of maximum switching rate and active display performance.

Projection Display employing addressable PDLCs

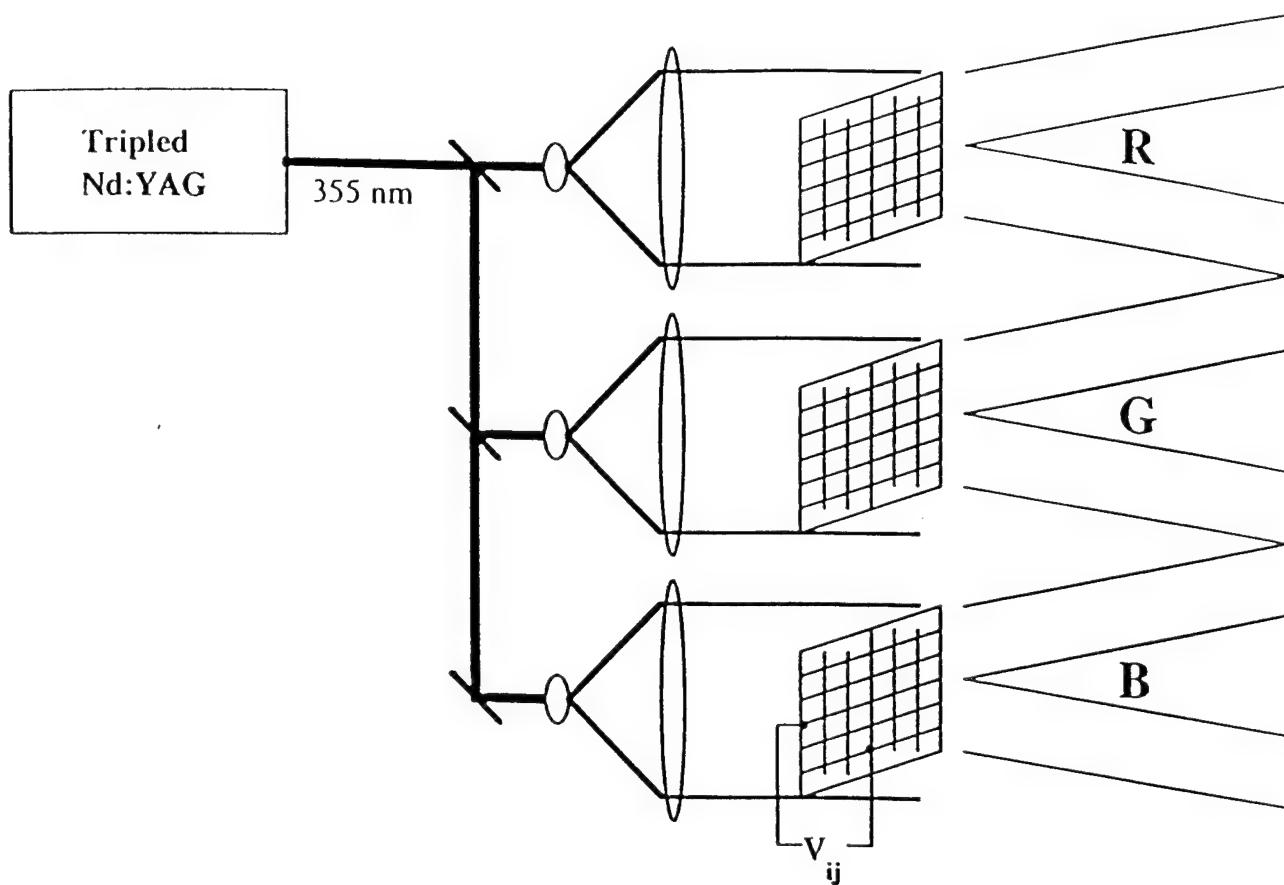


Figure 7.

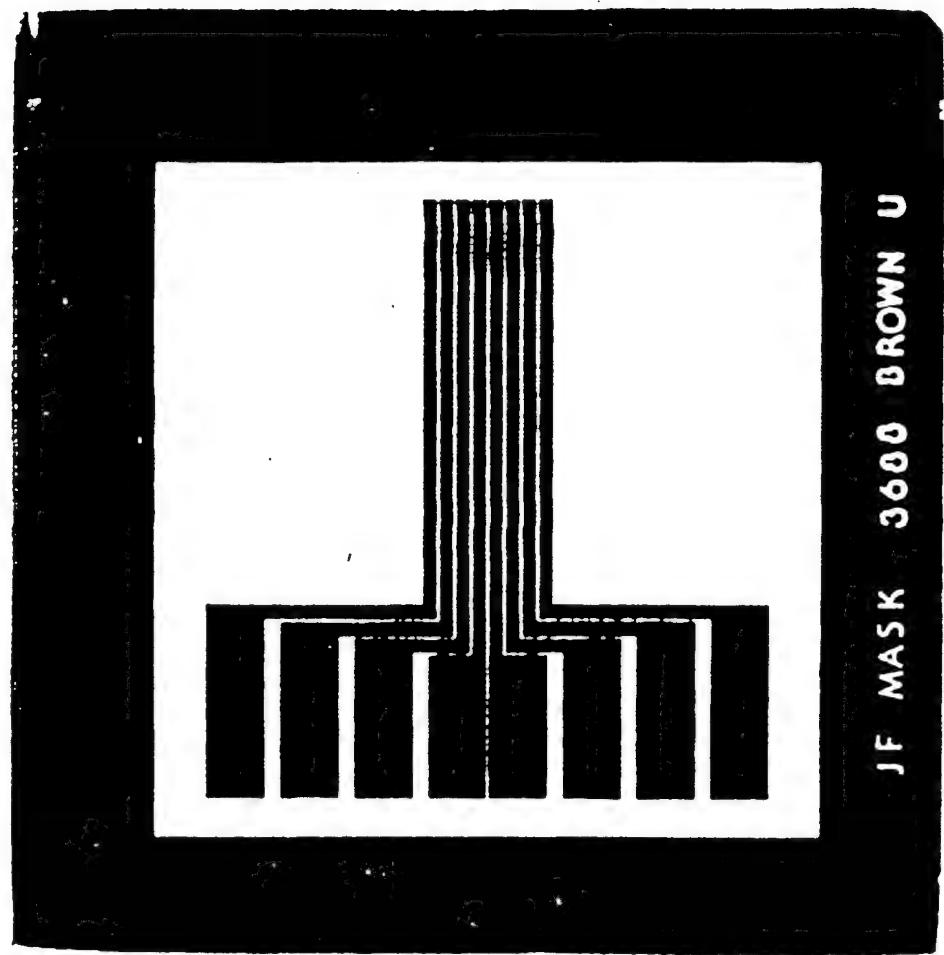


Figure 8.

III. Technical Feasibility

The technical feasibility of a video rate lasing display concerns:

- 1} Producing a low resolution ($<10^6$ pixels) video rate addressable lasing pixel array
and
- 2} The substitution of more robust solid state gain media for the flowing laser dye currently used.

The implementation of a video rate addressable array capability is expected to be straight forward with a high probability of success. The approach will utilize photolithographic patterning of ITO coated glass panels to switch the intracavity polymer dispersed liquid crystal (PDLC) shutters in an electronically selected spatial pattern. The first prototype will utilize a 300 x 300 cross line grid to define the pixels. The pixels will be actuated at a 30 Hz frame rate using a custom designed voltage driver circuit.

The successful completion of this version will be followed by the development of an active matrix liquid crystal lasing pixel array. This array is targeted to have over 10^6 pixels in a 2 inch diagonal array and will allow us to directly commercialize the technology for a number of applications. The most immediate commercial applications will be:

- 1} digital film transfer systems

2} conference room projection systems

3} special effects projection

In addition we expect that BMDO and other military display and tele-conferencing requirements may make immediate use of the technology.

We will maintain a flexible design approach which will smoothly allow us to substitute new, and less cumbersome solid state gain media. In particular, we will investigate the use of semiconducting polymer materials such as PPV and Meth-PPV for use as solid state gain materials. Lasing action in these materials has recently been demonstrated and the results indicate that they appear to be ideal high gain materials that can be utilized in a thin film design.^[2]

The development will focus on fabricating a low-to-medium resolution, video compatible PDLC shutter as a means of modulating the lasing output of each pixel. Simple images that can be switched at video rates will be demonstrated. Depending on the availability of the necessary driving electronics, direct-drive or multiplexing techniques will be employed to accomplish this task. Resolution is limited since the transmission versus voltage curve is gradual and therefore electrical coupling occurs between adjacent pixels which lowers contrast. Multiplexing uses the timing of the signals to select and write a particular line in the display. As more and more lines are written, the amount of time the controller can spend writing to each individual line (the duty cycle) decreases. Eventually, the molecules of liquid crystal do not have time to respond fully to

^[2] Tessler N., Denton G. J., and Friend R.H., Nature (382) 695 (1996).

the applied voltage, and contrast diminishes. Therefore any attempt to drive the display passively will be resolution limited.

Active matrix addressing is a technique for enhancing the addressing and writing of pixelated displays. The technique of active matrix addressing makes the display hardware more complicated by incorporating a switch at each pixel. The switch can be turned on and off very rapidly (microsecond regime) and a storage capacitor can then be used to maintain its condition while the other lines are being addressed. Several approaches to fabricating active matrix substrates have been investigated which include diodes, transistors, and various combinations thereof. Not only are many devices available, but there are many different materials to make the devices; the most popular being amorphous-silicon and poly-silicon. The poly-silicon active matrix substrates are currently being developed for small projection devices which would be the most interesting for the further development of an electrically controllable lasing device. Two US companies, Xerox and Kopin, are currently developing poly-silicon devices for projection devices. Very high resolutions are possible approaching 1200 by 1600 pixel arrays for 2-inch diagonal displays.

The final stage in developing an electrically controllable lasing device is to ultimately use an active matrix substrate with PDLC materials to achieve the highest possible resolution. Such a device would have great potential in the projection display market. The fastest route to developing an active matrix PDLC lasing device would be to take advantage of the currently designed poly-silicon active matrix substrates and drive technology and implement the PDLC material into this configuration. The current output of the drivers used in conjunction with poly-silicon devices is +/-6 volts. This is a challenge for PDLC materials since they typically turn on

between 6 and 8 volts. However, since our intention is to use them in projection based systems, the cell can be made thinner to lower the drive voltages without sacrificing too much contrast.

To execute a development program on a high resolution active matrix PDLC lasing display, it would be prudent to acquire a conventional poly-silicon active matrix display, drive electronics, and interface board from a US manufacturer. Since we are not using a conventional liquid crystal display, we would not require polarizers and would also request an empty cell. The empty cell would be filled with the low voltage PDLC material and sealed at Brown University. The high resolution PDLC display would be implemented into the lasing configuration stack (dichroic mirror, dye cell, PDLC silvered mirror plate) and evaluated at Spectra Science laboratories in Warwick, RI. This device is expected to serve as a prototype for demonstrating very high resolution lasing imaging at video rates.